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Measurement of radioactivity in building materials in Serbia

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Abstract This work presents a comprehensive study of natural radioactivity in 720 building materials imported in Serbia in 2012. Radioactivity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the studied samples range from <5 to 4,938, <3 to 763 and <10 to 3,192 Bq kg^{-1}, respectively. The maximum values of ^{226}Ra and ^{232}Th activity concentrations were found in zirconium mineral, while the highest ^{40}K activity concentration was in the feldspar. Based on the obtained radionuclide concentrations, radium equivalent activity, air absorbed dose rate, annual effective dose, external and internal hazard indices, gamma and alpha index due to radon inhalation were evaluated to assess the potential radiological hazard associated with these building materials.

Keywords Natural radioactivity · Dose assessment · Radium equivalent activity · Building materials

Introduction

All building materials contain various amounts of natural radioactive nuclides. Materials derived from rock and soil contain mainly natural radionuclides of the uranium (^{238}U) and thorium (^{232}Th) series, and the radioactive isotope of potassium (^{40}K). In the uranium series, the decay chain segment starting from radium (^{226}Ra) is radiologically the most important because the health effects of ^{238}U and the precursors of ^{226}Ra are negligible. It is well known that ^{226}Ra precursors are mostly alpha and beta emitter, while ^{226}Ra progeny have many gamma lines and therefore the reference is often made to radium instead of uranium. The world-wide average concentrations of radium, thorium and potassium in the earth's crust are about 40 Bq kg^{-1}, 40 Bq kg^{-1} and 400 Bq kg^{-1}, respectively [1]. Radioactive isotopes in building materials can increase both external and internal radioactive exposures of humans. Knowledge of the level of natural radioactivity in building materials is therefore important to assess the possible radiological hazards to human health and to develop standards and guidelines for the use and management of these materials. The worldwide average specific activity in the soil are given as follows: ^{226}Ra (32 Bq kg^{-1}), ^{232}Th (45 Bq kg^{-1}) and ^{40}K (420 Bq kg^{-1}), and in building materials: ^{226}Ra (50 Bq kg^{-1}), ^{232}Th (50 Bq kg^{-1}) and ^{40}K (500 Bq kg^{-1}) [2].

The purpose of setting controls on the radioactivity of building materials is to limit the radiation exposure due to materials with enhanced or elevated levels of natural radionuclides. The doses to the public should be kept as low as reasonably achievable. However, since small exposures from building materials are ubiquitous, controls should be based on exposures above typical levels and their normal variations.

Equations for alpha, gamma and hazard indices calculations.

By measuring the activity of radionuclides in building materials of unknown origin, or materials with addition of industrial waste, we were able to determine the compliance with regulations (that limit the maximum concentration of ^{226}Ra, ^{232}Th and ^{40}K). Gamma index for construction materials is calculated as follows [3]:

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Table 1 Maximum permissible concentration for ^{226}Ra, ^{232}Th and ^{40}K in buildings material used for interior, exterior and in civil engineering construction

Radionuclide	Label in the formula	MPC (maximum permissible concentration)		
		For interior (Article 13 in [3])	For exterior (Article 14 in [3])	In civil engineering construction (Article 15 in [3])
^{226}Ra	MPC(Ra)	300	400	700
^{232}Th	MPC(Th)	200	300	500
^{40}K	MPC(K)	3,000	5,000	8,000

$$I_\gamma = \frac{C_{Ra}(Bq\,kg^{-1})}{MPC(Ra)} + \frac{C_{Th}(Bq\,kg^{-1})}{MPC(Th)} + \frac{C_K(Bq\,kg^{-1})}{MPC(K)} \quad (1)$$

where C_{Ra}, C_{Th} and C_{K} are concentration and *MPC(Ra)*, *MPC(Th)* and *MPC(K)* are maximum permissible concentration of ^{226}Ra, ^{232}Th and ^{40}K respectively. Values of maximum permissible concentration depend on particular use of construction materials. These values for building materials used for interior, exterior and in civil engineering construction as a base for roads, playgrounds and other civil engineering construction (under the overlay layer) are presented in Table 1.

Gamma index must be less than 1 if material is to be used in high construction for interior. If the values obtained for the gamma index recalculated through the Eq. (1) meet the requirements for interior (Article 13 in [3]), then the material can also be used for exterior and civil engineering construction [3]. If the criterion for interior is not satisfied, then the calculation should be done according to Articles 14 and 15 [3].

The excess alpha radiation due to the radon inhalation originating from the building materials is assessed through alpha index which has to be less than 1 and is calculated according to the following equation [4]:

$$I_a = \frac{C(^{226}Ra)}{200} \leq 1 \quad (2)$$

where the recommended limit concentration of ^{226}Ra is 200 Bq kg^{-1} for which $I_\alpha = 1$.

The radium equivalent activity, Ra_{eq}, the absorbed gamma dose rate, $\dot{D}$, the annual effective dose, D_{E}, the external and internal hazard index, H_{ex} and H_{int}, were evaluated to assess the radiation hazard for people living in dwellings.

Radium equivalent activity, Ra_{eq}, can be calculated as follows [5, 6]:

$$Ra_{\mathrm{eq}} = C_{\mathrm{Ra}} + 1.43 \cdot C_{\mathrm{Th}} + 0.077 \cdot C_{\mathrm{K}} \quad (3)$$

The limit for Ra_{eq} is 370 Bq kg^{-1} set by the Organization for Economic Cooperation and Development (OECD 1979) report [7].

The absorbed gamma dose rate in indoor air, $\dot{D}$, and the annual effective dose, D_{E}, was calculated using the following equations [5]:

$$\dot{D} = 0.92 \cdot C_{\mathrm{Ra}} + 1.1 \cdot C_{\mathrm{Th}} + 0.08 \cdot C_{\mathrm{K}} \quad (4)$$

$$D_{\mathrm{E}} = 0.7 \cdot 7000 \cdot \dot{D} \quad (5)$$

The external hazard index H_{ex} is defined as [5]:

$$H_{\mathrm{ex}} = \frac{C_{\mathrm{Ra}}}{370} + \frac{C_{\mathrm{Th}}}{259} + \frac{C_{\mathrm{K}}}{4810} \quad (6)$$

In addition to the external radiation, radon and its short lived products are also hazardous to the respiratory organs. The internal exposure to radon and its daughter products is quantified by the internal hazard index H_{ex} which is given by the following equation [4]:

$$H_{\mathrm{in}} = \frac{C_{\mathrm{Ra}}}{185} + \frac{C_{\mathrm{Th}}}{259} + \frac{C_{\mathrm{K}}}{4810} \quad (7)$$

The value of these indices must be less than 1 in order to keep the radiation hazard insignificant.

Materials and methods

Before the measurements, the samples were crushed, sieved (mesh size 2 mm) to obtain homogeneity and placed in the plastic Marinelli beakers of 500 cm^3. The density of the samples ranged from 0.8 to 1.2 g cm^{-3}.

Two HPGe *p*-type detectors with relative efficiencies of 18 and 50 % and one *n*-type detector with relative efficiency of 20 % were used. Calibration of detectors was performed using silicone resin matrix spiked with a series of radionuclides (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{203}Hg, ^{88}Y, ^{113}Sn, ^{85}Sr and ^{137}Cs) with total activity of 41.48 kBq on the day thirty first August 2012 (Czech Metrological Institute, Praha, 9031-OL-420/12, type CBSS 2). The calibration was performed in the 500 cm^3 Marinelli beaker geometry, too. For efficiency calibration of samples having different density compared to resin, two additional secondary reference materials were produced in accordance with IAEA recommendations [8]. These are charcoal and sand in Marinelli beaker, spiked with standard radioactive solution ER X 9031-OL-426/12 issued by Czech Metrological Institute, Inspectorate for Ionizing Radiation. The radioactive solution contained following radionuclides: ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{203}Hg, ^{113}Sn, ^{85}Sr and ^{88}Y, with the energies that span from 59 to 1,898 keV with total activity of 1,342 Bq at reference date 31.08.2012.

Table 2 The concentration of ^{226}Ra, ^{232}Th and ^{40}K in building material which fulfilled 100 % criterion for interior

Sample	No		^{226}Ra	^{232}Th	^{40}K	$I\gamma$ (interior) < 1 (%)
Bentonite	15	min-max	22–84	42–86	223–629	100
		Average	35 ± 16	68 ± 10	530 ± 100	
Cement	22	min-max	8–89	<3–131	<10–182	100
		Average	37 ± 22	15 ± 29	43 ± 64	
Dolomite	7	min-max	<5–25	<3–<7	<10–<30	100
		Average	12 ± 10			
Gypsum	265	min-max	<5–260	<3–44	<10–271	100
		Average	20 ± 26	0.4 ± 3	23 ± 55	
Clay	3	min-max	11–91	<3–67	<10–555	100
		Average	47 ± 41	37 ± 34	280 ± 280	
Talc	4	min-max	<5–48	<3–36	<10–124	100
		Average	12 ± 24	9 ± 18	41 ± 58	
Limestone	66	min-max	7–227	<3–<7	<10–62	100
		Average	84 ± 44		14 ± 10	
Marble	7	min-max	<5–40	<3–<7	<10–<30	100
		Average	17 ± 16			

Table 3 The concentration of ^{226}Ra, ^{232}Th and ^{40}K in building material which not fulfilled criterion for interior

Sample	No		^{226}Ra	^{232}Th	^{40}K	$I\gamma$ (interior) < 1 (%)	$I\gamma$ (exterior) < 1 (%)
Zirconium mineral	15	min-max	4,746–4,938	673–763	<10–< 30	0	0
		Average	4,840 ± 40	718 ± 64			
Feldspar	42	min-max	<5–158	<3–163	<10–3,192	93	7
		Average	54 ± 29	69 ± 40	320 ± 760		
Granite	211	min-max	<5–430	<3–444	<10–2,172	81	14
		Average	38 ± 52	43 ± 57	660 ± 540		
Stone	26	min-max	<5–103	<3–69	<10–1,277	92	8
		Average	30 ± 31	11 ± 23	250 ± 430		
Kaolinite	15	min-max	32–156	20–146	82–1,061	67	33
		Average	80 ± 40	71 ± 41	380 ± 250		
Silica sand	14	min-max	<5–94	<3–385	<10–340	86	7
		Average	21 ± 24	61 ± 120	46 ± 95		
Sand	9	min-max	<5–97	<3–90	<10–1,100	89	11
		Average	26 ± 41	30 ± 35	210 ± 380		
Tile	3	min-max	93–133	66–83	838–1,053	33	67
		Average	110 ± 21	77 ± 10	940 ± 110		

The spectra were analyzed using the program GENIE 2,000. The activity of ^{226}Ra and ^{232}Th was determined by their decay products: ^{214}Bi (609, 1,120 and 1,764 keV), ^{214}Pb (295 and 352 keV) and ^{228}Ac (338 and 911 keV), respectively. The activities of ^{40}K and ^{137}Cs were determined from its 1,460 and 661 keV γ-energy, respectively. The background spectrum was recorded regularly after or before the sample counting.

Relative measurement uncertainty for the experimental values was calculated according to the following Equation:

$$u(\varepsilon) = \sqrt{(\delta A)^2 + (\delta N)^2 + (\delta M)^2 + (\delta P)^2} \quad (8)$$

where δA represents relative uncertainty of the radioactive solution given by the manufacturer, δN is the relative counting uncertainty, δM is the uncertainty introduced in the process of production of the secondary reference material and δP represent other components such as the sample position and "run to run" uncertainty. $\delta A + \delta M$ is estimated to be approximately 2–3 %, while δP is

Table 4 The radium equivalent activity, the absorbed gamma dose rate, the annual effective dose and external and internal hazard index for building materials

Building material		Ra_{eq} (Bq kg^{-1})	$\dot{D}$ (nGyh^{-1})	D_E (mSv)	H_{ex}	H_{int}	I_a
	MIN	141	126	0.62	0.38	0.46	0.11
Bentonite	MAX	227	195	0.96	0.61	0.77	0.42
	AVERAGE	172	149	0.73	0.46	0.56	0.17
	MIN	10	9	0.04	0.03	0.04	0.04
Cement	MAX	282	232	1.14	0.76	1.00	0.45
	AVERAGE	62	54	0.27	0.17	0.27	0.19
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Dolomite	MAX	25	23	0.11	0.07	0.14	0.13
	AVERAGE	12	11	0.05	0.03	0.06	0.06
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Feldspar	MAX	274	255	1.25	0.74	1.11	0.79
	AVERAGE	177	151	0.74	0.48	0.62	0.27
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Gypsum	MAX	260	239	1.17	0.70	1.41	1.30
	AVERAGE	23	21	0.10	0.06	0.12	0.10
	MIN	11	10	0.05	0.03	0.06	0.06
Clay	MAX	210	181	0.89	0.57	0.81	0.46
	AVERAGE	122	107	0.52	0.33	0.46	0.24
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Stone	MAX	272	247	1.21	0.73	0.94	0.52
	AVERAGE	65	60	0.29	0.18	0.26	0.15
	MIN	10	9	0.04	0.03	0.04	0.04
Limestone	MAX	227	209	1.02	0.61	1.23	1.14
	AVERAGE	85	78	0.38	0.23	0.46	0.42
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Marble	MAX	40	37	0.18	0.11	0.22	0.20
	AVERAGE	17	16	0.08	0.05	0.09	0.09
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Sand	MAX	308	274	1.34	0.83	1.09	0.49
	AVERAGE	85	74	0.36	0.23	0.30	0.13
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Granite	MAX	879	724	3.55	2.37	2.77	2.15
	AVERAGE	150	134	0.66	0.40	0.51	0.19
	MIN	84	72	0.35	0.23	0.33	0.16
Kaolinite	MAX	355	303	1.49	0.96	1.34	0.78
	AVERAGE	210	181	0.89	0.57	0.78	0.40
	MIN	<10	<9	<0.04	<0.03	<0.04	<0.03
Silica sand	MAX	645	510	2.50	1.74	1.99	0.47
	AVERAGE	111	90	0.44	0.30	0.36	0.10
	MIN	252	225	1.10	0.68	0.93	0.47
Tile	MAX	333	298	1.46	0.90	1.26	0.67
	AVERAGE	292	261	1.28	0.79	1.09	0.55

estimated to 2 %. Relative measurement uncertainty $u(\varepsilon)$ for all energies did not exceed 10 % at 2σ level of confidence.

Results

The building materials were gathered from different regions of Serbia or imported from other countries and analyzed by gamma spectrometry to quantify radioactivity concentrations using high purity germanium detector. The largest quantity of imported samples were cement, gypsum, granite, stone, clay, ceramic tiles and zirconium minerals.

The range (minimum and maximum) and average concentration of ^{226}Ra, ^{232}Th and ^{40}K measured in 720 building material in 2012 are presented in Tables 2 and 3. The building materials which fulfilled 100 % criterion for interior are presented in Table 2, while the results for other building materials are presented in Table 3. All materials presented in Table 3 except zirconium mineral and granite fulfilled criterion for exterior. For the granite 4 % samples obtained certificate for using in civil engineering construction as a base for roads, playgrounds and other civil engineering construction (under the overlay layer), while 1 % of granite material were rejected. According to Serbian regulations [3] gamma index is applied to any building material and its additives. Zirconium mineral is an additive and its index has to be calculated too. As the zirconium mineral is used as component in the recipe for the production of ceramics, therefore a disclaimer from the client was obtained, stating the purpose of using the zirconium mineral and the percentage in which it will be used in the production process. The zirconium mineral is used as component in concentration not above 3 % [9] and in that case all zirconium mineral samples obtained certificate for interior.

The radium equivalent activity, Ra_{eq}, the absorbed gamma dose rate, $\dot{D}$, the annual effective dose, D_E, the external and internal hazard index, H_{ex} and H_{int}, are presented in Table 4. The results for zirconium mineral in Table 4 are omitted because the zirconium mineral is used only as a small component of some building materials.

Conclusion

^{226}Ra, ^{232}Th and ^{40}K activity concentration were measured in building materials using gamma spectrometry. The highest ^{226}Ra and ^{232}Th activity concentrations were found in zirconium mineral, 4,938 and 763 Bq kg^{-1}, respectively. The maximum ^{40}K activity concentration was 3,192 Bq kg^{-1} in the feldspar. The radium equivalent activities ranged from 10 to 355 Bq kg^{-1} in all building materials except granite in which the radium equivalent activity maximum was up to 879 Bq kg^{-1}. The alpha index was from <0.03 to 0.79 in all samples except gypsum and granite, where maximum values were 1.3 and 2.15, respectively.

According to Serbian regulations gamma index is applied to any building material and its additives. The present study shows that the measured bentonite, cement, dolomite, gypsum, clay, talk, limestone and marble fulfilled 100 % criterion for dwelling construction. The measurement in other construction materials, such as feldspar, granite, stone, kaolinite, silica sand, sand and tiles showed that only 80 % samples fulfilled the criterion for dwelling construction, 18.5 % samples meet the criteria for the exterior usage and the rest of 1.4 % samples could be used in civil engineering construction as a base for roads, playgrounds and other civil engineering construction (under the overlay layer) and 0.1 % materials were rejected. Some material, for example zirconium mineral, which is used as component in small concentration, also obtained certificate for dwelling construction, although the all alpha, gamma and hazard indices were very high.

The results of activity concentration measurements in building materials used in construction industry in Serbia allows the authors to conclude that almost all measured samples could be safely used in building constructions.

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References

1. European Commission (1999) Radiological protection principles concerning the natural radioactivity of building materials. Radiation Protection 112. EC, Luxembourg
2. UNSCEAR (2008) Sources and effects of ionizing radiation. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York
3. RS Official Gazette (2011) Rulebook on limits of radionuclides content in drinking water, foodstuffs, feeding stuffs, medicines, general use products, construction materials and other goods that are put on market. Official Gazette of the Republic of Serbia No 86. National Assembly of the Republic of Serbia, Belgrade
4. Eštoková A, Palaščáková L (2013) Assessment of natural radioactivity levels of cement and cement composites in the slovak republic. Int J Environ Res Public Health 10:7165–7179
5. Todorović D, Janković M (2012) Natural radioactivity of materials used in industry and construction in Serbia. Int J Environ Sci Health Part A 46:1147–1153
6. Muntaean LE, Cosma C, Moldovan DV (2014) Measurement of natural radioactivity and radiation hazards for some natural and artificial building materials available in Romania. J Radioanal Nucl Chem 299:523–532
7. OECD (1979) Exposure to radiation from the natural radioactivity in building materials. Report by a Group Experts of the OECD Nuclear Energy Agency, Organization for Economic Cooperation and Development, Paris

8. Vukanac I, Djurasevic M, Kandic A, Novkovic D, Nadjerdj L, Milosevic Z (2008) Experimental determination of the HPGe spectrometer efficiency curve. Appl Radiat Isotop 66:792–795
9. Janković MM, Todorović DJ (2011) Concentrations of natural radionuclides in imported zirconium minerals. Nucl Techn Radiat Prot 26:110–114